DETERMINATION OF PROTONATED AND QUATERNARY CARBONS IN H-COAL LIQUIDS FROM QUATERNARY CARBON SUPPRESSED AND NONSUPPRESSED CMR SPECTRA

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INTRODUCTION

The potentially rapid and accurate measurement of the carbon distribution by structural types in a coal liquid is an attractive application of ^{13}C FT-NMR spectroscopy. Extensive CMR work has been carried out in many laboratories[1] on coal-derived liquids. As part of a continuing program to study the physicochemical properties of the H-Coal liquids to provide analytical support for the commercial development of the H-Coal process[2], we have made further application of quantitative FT-CMR technique to determine the distribution of several types of aliphatic and aromatic carbons in three H-Coal liquids. In order to confirm the interpretation of the highly complex spectra based on chemical shifts, use has been made of the difference in CMR absorptivity of protonated and quaternary carbons as a means to distinguish between them. We have demonstrated the reliability of this difference by comparing the quantitative CMR spectrum of a simulated coal liquid containing 30 peaks (15 each in the aliphatic and aromatic region) with the spectrum of the same mixture obtained with a Fourier transform parameter set wherein the quaternary carbons are suppressed. This difference CMR technique has been applied to three H-Coal liquids: atmospheric still overhead (ASO), atmospheric still bottom (ASB), and vacuum still overhead (VSO). There is no discernible amount of aliphatic quaternary carbon found in these liquids. In the aromatic region, the ring carbons are divided into six subgroups by ring substitutions. The three liquids are thus compared by structural classification and quantitation of their CMR spectra.

EXPERIMENTAL

The liquefied coal samples under investigation were received from the Institute for Mining and Minerals Research, University of Kentucky. The liquefaction was performed by the H-Coal process involving a catalyst in the "syncrude" mode with reactor temperature at 454°C, exit reactor partial pressure of hydrogen at 2245 psig. The samples were designated atmospheric still overhead (ASO), atmospheric still bottom (ASB), and vacuum still overhead (VSO). The nominal boiling ranges of these samples are ASO C_4 - 200°C, ASB 200-350°C, VSO 350-520°C[2]. Chemicals were purchased from Aldrich Chemical Co.

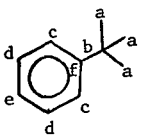
A Bruker WH-90DS nuclear magnetic resonance spectrometer with a 10 mm probe and a Nicolet BNC 1180 computer (16 K memory) was used in the Fourier transform mode to obtain the ^{13}C spectra at 22.63 MHz. The FIDs were accumulated on 8K memory, using an acquisition time of 0.819s. A 5000 Hz spectral width with 200 microseconds dwell time was used in all spectra. The quantitative spectra were obtained at 30° pulse width with 5s delay between the end of data acquisition and the beginning of the next pulse for $\sim$10,000 pulses. During the delay, the proton spin decoupler was gated off, but a 5.0 watt decoupling power was applied while scanning. The relaxation agent $Cr(acac)_3$ was used at 20 mg/g of sample. For the quaternary carbon-suppressed spectra, the following FT parameters were adopted: 90° pulse width, no pulse delay, broad band proton decoupling at 5.0 watt for $\sim$10,000 scans, and no paramagnetic relaxation agent added.

The H-Coal samples were prepared by adding 1.0 g of of the respective coal liquid to 1 ml of $CDCl_3$ containing 1% of tetramethylsilane. The solvent $CDCl_3$ also served the purpose of internal deuterium lock. For the simulated coal liquid, the following mixture was made up: t-butylbenzene (69.0 mg, 0.515 mmol), decalin (77.2 mg, 0.559 mmol), tetralin (77.5 mg, 0.587 mmol), 2-phenylpentane (76.4 mg, 0.516

mmol), and 2,3-dimethylnaphthalene (75.9 mg, 0.487 mmol), and $CDCl_3$ was added to make a 2 ml solution. When the spectra were calibrated for integration, a weighed amount of dioxane in a sealed capillary tube was placed along the axis of the 10 mm nmr tube with the aid of a vortex-type plug.

RESULTS AND DISCUSSION

The quaternary carbons which are devoid of protons in their immediate vicinity, hence lacking the $^{13}C - {}^{1}H$ dipole-dipole relaxation mechanism, are expected to have long spin-lattice relaxation recovery times (T_1). This makes the signal intensity very dependent on the pulse repetition rate. The presence of nuclear Overhauser enhancement (NOE) for the protonated carbons further accentuates the difference in absorptivity between these two types of carbons. Thus, in a normal broad band proton decoupled CMR spectrum, the quaternary carbons show much reduced signal intensities relative to others. We have quantitated the differences in absorptivity for carbons with various levels of proton attachment (1°, 2°, 3°, and 4°) using a simulated coal liquid (Cf. Experimental). This mixture is comprised of 25 aliphatic carbons (primary 7, secondary 14, tertiary 3, and quaternary 1) and 28 aromatic carbons (protonated 20 and quaternary 8) as shown below. The aromatic and aliphatic



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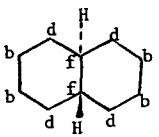

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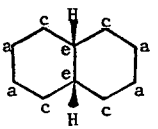

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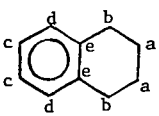

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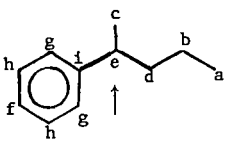

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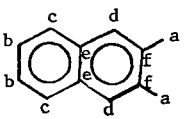

V

regions of this spectrum are shown in Figures 1A and 2A respectively. This set of FT parameters tend to equalize all signal intensities per carbon unit irrespective of their molecular environment. Thus, the one aliphatic and eight aromatic quaternary carbons were separately integrated to yield absolute value within 5% deviation from the theoretical. On the other hand, when the spectrum was taken in the absence of $Cr(acac)_3$ using broad band decoupling at 90° pulse width and no delay, vast variations of the signal intensities including suppression of the quaternary carbons were registered. The respective aromatic and aliphatic regions shown in Figures 1B and 2B reveal the differences from those in Figures 1A and 2A. In order to quantitate these changes, the height of each peak in both spectra was normalized to either the tallest peak at δ125.47 (protonated carbons IIIc and Vb) or to an internal standard of dioxane. The normalized peak height of each peak in the quantitative spectrum is expressed as a ratio to that of the same derived from the quaternary carbon suppressed spectrum to show the signal intensity changes in the latter spectrum. These reults are shown in Table I. It can be seen that the two columns of peak height ratios point to the same trend and agree to within 7% of deviation. Thus, the dioxane methylene carbons and the aromatic methine carbons IIIc and Vb exhibit similar relaxation characteristics and are both adequate as integral references. In the

nonquantitative spectrum, the eight quaternary aromatic carbons appearing in 5 peaks average a 5 fold decline. The twenty protonated carbons in ten peaks increase by ∿20% per carbon. The single aliphatic quaternary carbon is suppressed 4.7 fold, while the 14 peaks representing 3 tertiary, 14 secondary, and 7 primary aliphatic carbons average an increase of 0%, 37%, and 43% per carbon respectively. Although these peak enhancements of various protonated carbons are similar, hence not diagnostic of the extent of proton attachment, it is demonstratably clear that the quaternary carbons can be confirmed by this difference CMR method due to their pronounced peak height changes.

Thus, the H-Coal liquids ASO, ASB, and VSO were submitted to close examination by the difference CMR technique. The comparisons for the aromatic and aliphatic regions are shown in Figures 3 and 4 respectively for ASO, Figures 5 and 6 for ASB, and Figures 7 and 8 for VSO. In each figure, spectrum A is the quantitative type and B the quaternary carbon-suppressed type. Those peaks which have disappeared or declined in intensity by at least 3.8 fold for ASO and ASB and at least 2 fold for VSO are assigned to the quaternary aromatic compounds either as bridge carbons in a condensed ring system or carbons to which alkyl or aryl substituents are attached. The remainder of the aromatic resonances therefore belong to the protonated carbons. It is interesting to note that the aliphatic regions for all three liquids show no discernible difference when the two types of spectrum are compared, indicating the absence of quaternary branching in the saturated carbon skeletons.

The chemical shifts of unsubstituted carbons in mono, di, tri, and tetra aromatic ring systems fall in a narrow range of 123 - 130 ppm[3,4]. When the benzene ring bears heteroatom substituent such as OH or OR, the protonated carbons are shifted upfield considerably, e.g. to 113 ppm in m-cresol and to 106 ppm in benzofuran[5]. In the region of 130-133.8 ppm, most of the condensed-ring bridge carbons can be found[3,4]. However, in a highly condensed system such as pyrene, the interior bridge carbons resonate at 125 ppm due to the anisotropic ring current effect[3]. The 133.8 - 137.3 ppm region is appropriate for substituted carbons in tetralin and methylbenzenes[3,5]. Short chains (Et, Pr, iPr, etc.) tend to shift the substituted carbons downfield to 149 ppm[3,5]. Also, an alkyl substituent at C-8 in tetralin and particularly gem-substituted tetralins can bring the bridge carbon C-8a to the 140's[3]. Biphenyls also appear in this region[5]. Beyond 149 ppm, the aromatic carbons carrying a heteroatom group such as OH or OR appear[1c,5]. Such chemical shift analysis in combination with the difference CMR method to determine the quaternary and protonated carbons permit a reasonable interpretation of the aromatic resonances in the H-Coal liquids. In Table II, the distribution of the aromatic carbons in ASO, ASB, and VSO are shown as obtained from the integration of the chemical shift regions indicated. The one quaternary carbon detected in ASO at 127.1, at 124.4 in ASB and at 124.7 in VSO may be attributed to highly condensed interior carbon. The absence of other reduced signals in the 123 - 130 ppm region confirms the assignment of this region to the protonated carbons. The patterns of the distribution of aromatic carbons in the three liquids generally denote the more condensed ring systems with higher branchings in the VSO liquid, whereas ASO and ASB are more similar.

ACKNOWLEDGEMENT

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Table I. Ratios of Carbon Peak Heights from Quantitative and Quaternary Carbon Suppressed CMR Spectra of the Simulated Coal Liquid[a]

A. Aromatic Region

Peak No	δ TMS = 0	Assignment[b] Notation	Carbon Type	Peak Height Ratios Internal Reference[c]	Dioxane Reference[d]
1	151.0	If	4^o	6.4	6.1
2	147.9	IVi	4^o	5.7	5.4
3	137.1	IIIe	4^o	4.5	4.2
4	135.4	Vf	4^o	4.2	3.9
5	132.5	Ve	4^o	5.4	5.1
6	129.1	IIId	3^o	1.0	1.0
7	128.3	IVh	3^o	0.8	0.7
8	128.1	Ie	3^o	1.0	1.0
9	127.4	Vd	3^o	0.8	0.7
10	127.0	IVg	3^o	0.9	0.8
11	126.9	Vc	3^o	0.8	0.8
12	125.8	IVf	3^o	0.9	0.9
13	125.5	IIIc,Vb	3^o,3^o	1.0	0.9
14	125.3	Id	3^o	1.0	1.0
15	125.0	Ic	3^o	0.8	0.8

B. Aliphatic Region

16	43.5	IIf	3^o	1.2	1.1
17	40.8	IVe	3^o	0.8	0.7
18	39.7	IVd	2^o	0.9	0.6
19	35.4	IIe	3^o	1.3	1.2
20	34.6	Ib	4^o	5.0	4.7
21	34.3	IId	2^o	0.8	0.8
22	31.3	Ia	1^o	0.7	0.7
23	29.4	IIb,IIc	2^o,2^o	0.8	0.7
24	26.8	IIb	2^o	0.9	0.8
25	24.8	IIa	2^o	0.9	0.9
26	23.3	IIIa	2^o	0.7	0.6
27	22.3	IVc	1^o	0.7	0.6
28	20.9	IVb	2^o	0.7	0.7
29	20.1	Va	1^o	1.0	0.9
30	14.2	IVa	1^o	0.7	0.6

[a] A mixture of t-butylbenzene (I), decalin (II, cis:trans 1:4) tetralin (III), 2-phenylpentane (IV) and 2,3-dimethylnaphthalene (V) was made up in mole fractions of 0.1955, 0.2105, 0.2180, 0.1955 and 0.1805 respectively.

[b] According to The Sadtler Standard Carbon-13 NMR Spectra[6b]

[c] Peak heights are normalized to the tallest peak at δ125.47 (protonated carbons, IIIc and Vb)

[d] Peak heights are normalized to the capillary dioxane peak. Refer to footnote a in Table I.

Table II. Distribution of Aromatic Carbons in H-Coal Liquids by Structural Types

Benzene Ring Carbon Types	Chemical Shift Range, ppm	% Distribution ASO	ASB	VSO
CH, OR subst.	111-123	3.4	12.0	9.7
CH, Unsubst.	123-130	53.0	49.2	46.1
CR, Condensed bridge	130-133.8	11.7	11.4	14.9
CR, Tetralin & Me Subst.	133.8-137.3	13.4	11.5	10.4
CR, Aryl & Branched Alkyl	137.3-149	18.5	15.9	18.8
C-OR	149-160	a	b	b

[a] No discernible signals are found.
[b] A few low intensity signals are observed but they are too small to integrate.

Figure 1 Aromatic Regions of the Quantitative (A) and Quaternary Carbon Supressed (B) CMR Spectra of the Simulated Coal Liquid.

Figure 2 Aliphatic Regions of the Quantitative (A) and the Quaternary Carbon Suppressed (B) CMR Spectra of the Simulated Coal Liquid.

Figure 3 Aromatic Regions of Quantitative (A) and Quaternary Carbon Suppressed (B) CMR Spectra of ASO.

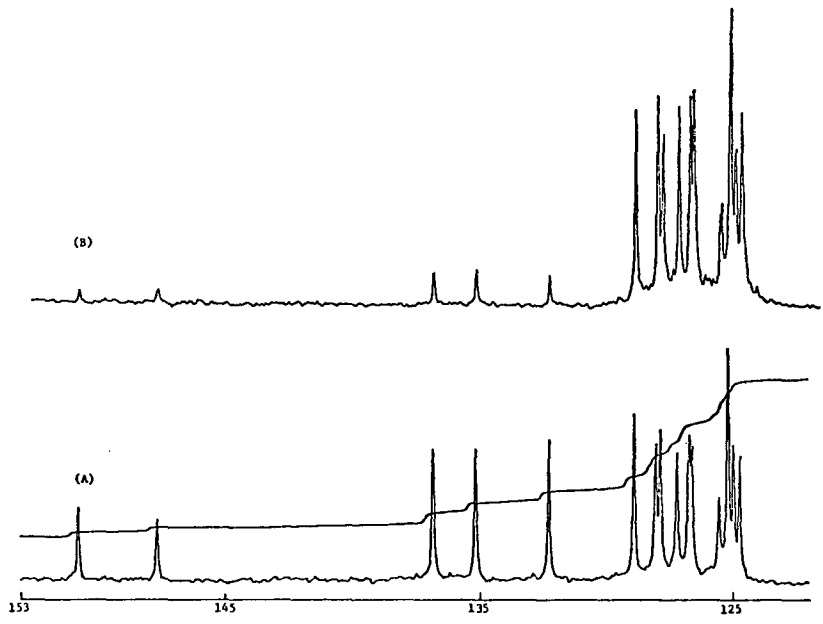
Figure 4 Aliphatic Regions of Quantitative (A) and Quaternary Carbon Suppressed (B) CMR Spectra of ASO.

Figure 5 Aromatic Regions of the Quantitative (A) and Quaternary Carbon Suppressed (B) Spectra of ASB

Figure 6 Aliphatic Regions of the Quantitative (A) and Quaternary Carbon Suppressed (B) CMR Spectra of ASB

Figure 7 Aromatic Regions of the Quantitative (A) and Quaternary Carbon Suppressed (B) CMR Spectra of VSO

Figure 8 Aliphatic Regions of the Quantitative (A) and Quaternary Carbon Suppressed (B) CMR Spectra of VSO



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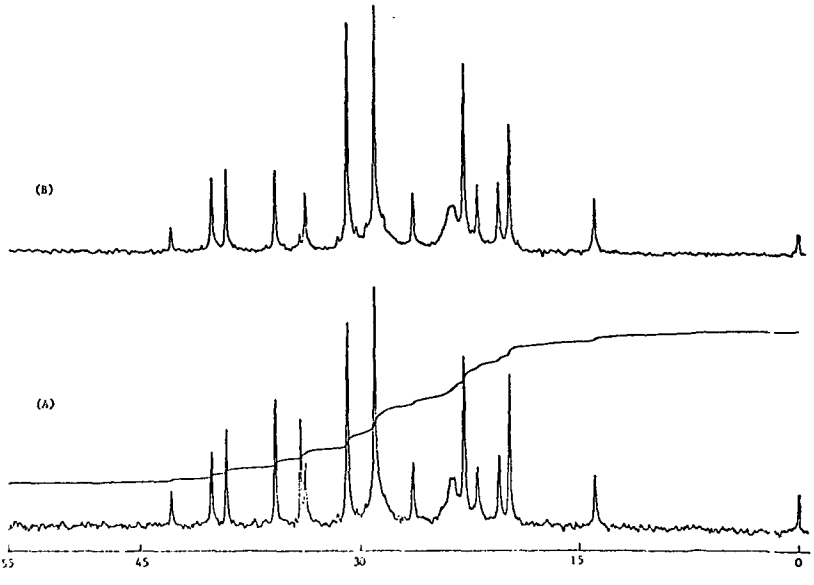

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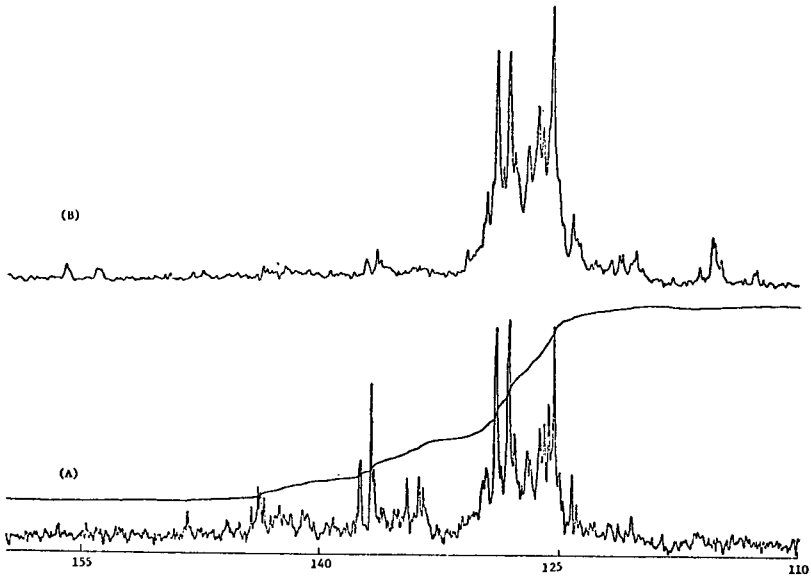

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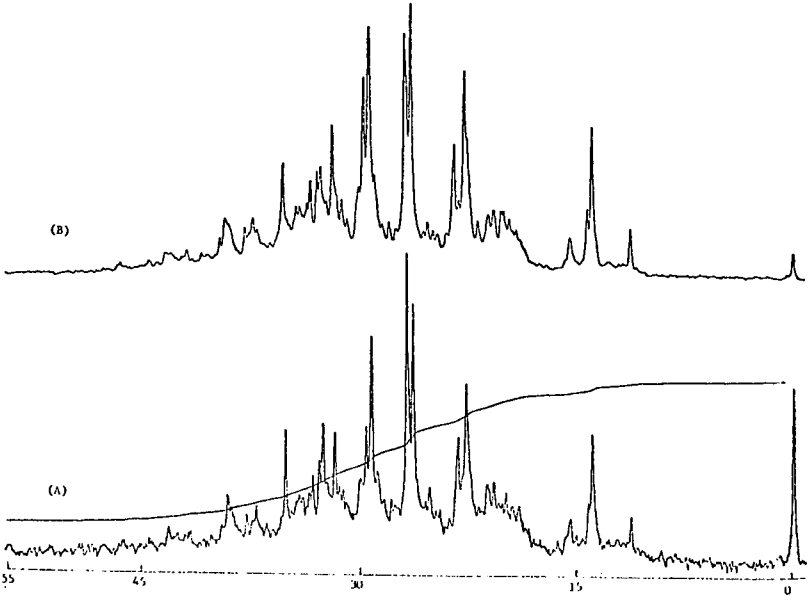

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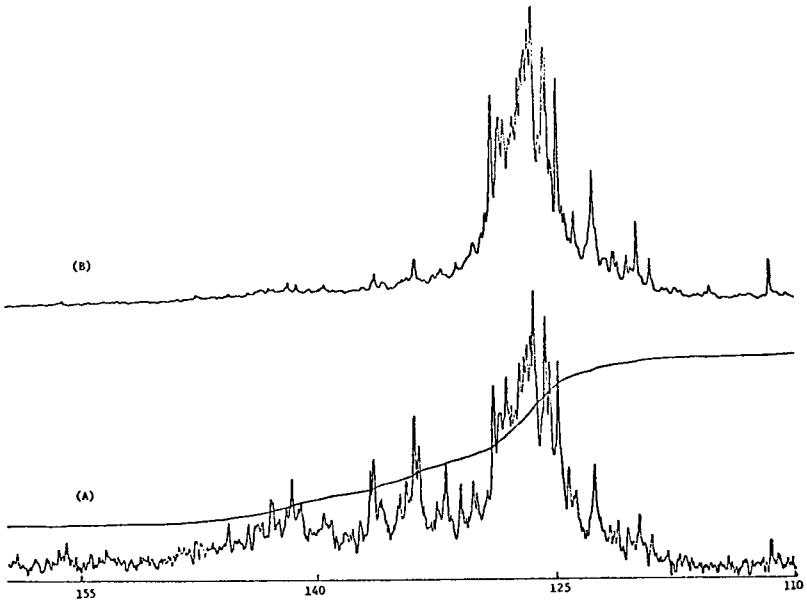

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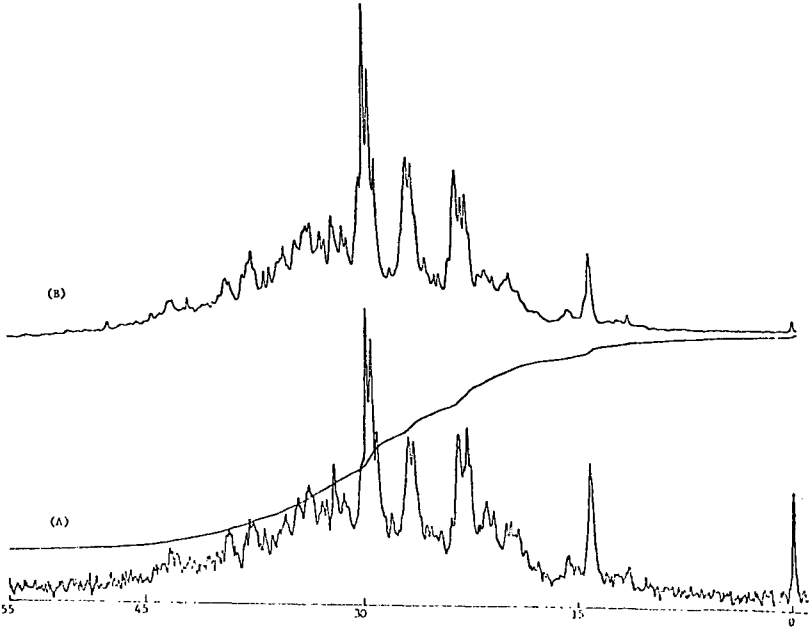

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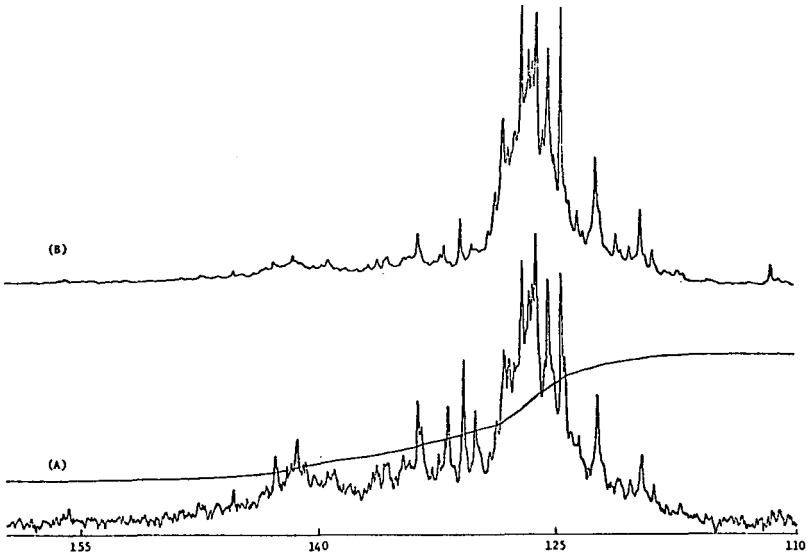

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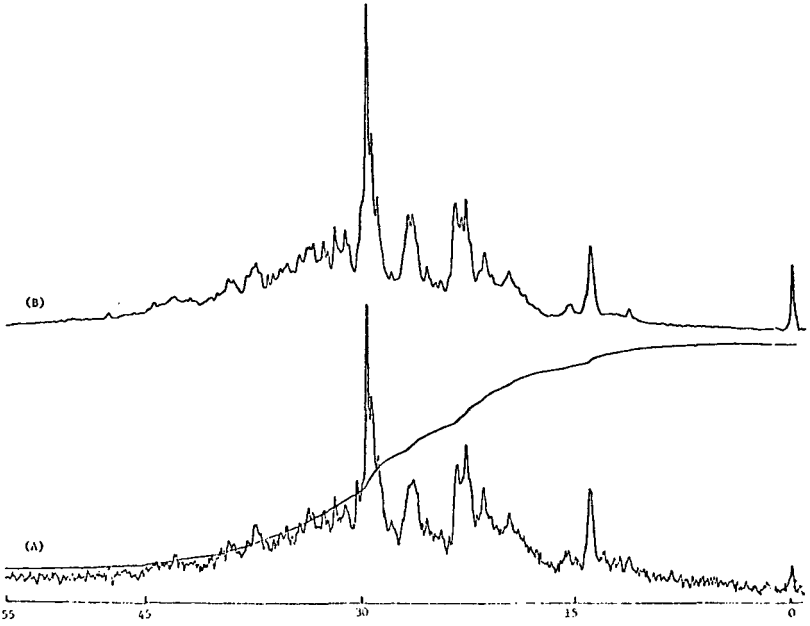

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